

Review

# Exploring Humic Acid as an Efficient and Selective Adsorbent for Lead Removal in Multi-Metal Coexistence Systems: A Review

Shuwen Xue <sup>1</sup>, Yunhu Hu <sup>1</sup>, Keji Wan <sup>2,\*</sup>  and Zhenyong Miao <sup>3,\*</sup>

<sup>1</sup> School of Chemistry and Materials Engineering, Huainan Normal University, Huainan 232001, China; xueshuwen@cumt.edu.cn (S.X.); huyunhu@ustc.edu.cn (Y.H.)

<sup>2</sup> National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, China

<sup>3</sup> School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China

\* Correspondence: wankeji@cumt.edu.cn (K.W.); zymiao@cumt.edu.cn (Z.M.)

**Abstract:** Water pollution poses a global threat to human health, particularly in terms of ensuring a safe supply of drinking water. The accumulation of heavy metals from various water sources is increasing, driving the search for effective and environmentally friendly approaches and materials for metal removal. This review investigates the selective adsorption of Pb<sup>2+</sup> by humic acid (HA) in a multi-metal coexistence solution. The focus is on discussing approaches to the structural identification of HA, highlighting that separation techniques are an effective method to reduce its heterogeneity. Starting from the key structural units of HA, the study reveals the interaction between HA and heavy metals. Approaches to enhance Pb<sup>2+</sup> selective adsorption are explored, proposing that introducing activating groups, Ca ion exchange, and optimizing pore structures are effective approaches for improving lead ion selective adsorption. Ca<sup>2+</sup> activation is suggested as a future research direction for lead-selective adsorption. Additionally, attaining lead selective adsorption through pH regulation's significance is emphasized. This research contributes to a fundamental understanding of HA's role as a selective lead adsorbent while offering practical implications for developing environmentally friendly adsorbent materials. The results aim to advance knowledge in environmental science and water treatment.

**Keywords:** humic acid; fractionation; structural identification; selective adsorption; modification method



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## 1. Introduction

Water, as the primary constituent of life on Earth, is confronted with persistent challenges to its quality and quantity due to urbanization, industrialization, and the growing global population. The emission of toxic heavy metals, such as lead, has reached substantial levels, with approximately 350,000 tons of Pb released per million tons of emissions [1]. Various industrial processes contribute to the release of Pb, leading to severe water pollution. Wastewater containing Pb<sup>2+</sup> poses a significant threat to aquatic ecosystems and human health. Upon entering the human body, lead can adversely affect various organs, resulting in pathological changes. Elevated lead levels in the body can lead to detrimental effects on the brain, kidneys, and reproductive system. The impact on nerve cell myelin can impair muscular functions. Environmental protection standards, such as those set by the Environmental Protection Agency (EPA) and the World Health Organization (WHO), dictate that the Pb<sup>2+</sup> content in drinking water should not exceed 0.015 mg L<sup>-1</sup> and 0.01 mg L<sup>-1</sup>, respectively [2,3]. The current challenges in treating lead-contaminated wastewater mainly include high toxicity and low permissible limits, low pH, the complexity of wastewater, cost, as well as sustainability and waste management.

In response to these challenges, ongoing research and development efforts are focused on identifying more efficient, cost-effective, and sustainable methods for the removal of lead from wastewater. These include precipitation [4], electrolysis [5], adsorption [6], photocatalysis [7], membrane separation [8], and fenton-like oxidation [9], which are employed in water treatment. Precipitation methods currently stand as the primary treatment approach for acidic lead-containing wastewater. However, conventional chemical precipitation methods exhibit concentration limitations. Post-precipitation effluent fails to meet national discharge standards, and challenges persist in solid–liquid separation, posing obstacles to achieving comprehensive purification of lead-containing wastewater. Electrochemical methods can efficiently remove lead at low concentrations, but they have high energy consumption. Membrane filtration methods can remove a wide range of pollutants, including  $\text{Pb}^{2+}$ , to below detectable limits, but membrane fouling reduces efficiency and increases costs. Fenton-like oxidation technology can rapidly and multi functionally treat lead-contaminated wastewater, but it generates sludge, increasing the cost and complexity of the wastewater treatment process. Compared to other heavy metal treatment methods, adsorption offers greater diversity and applicability, reversibility [10], low cost, ease of operation, and efficiency [11]. Therefore, it is widely applied and highly regarded in the field of water treatment. However, the efficiency and cost-effectiveness of adsorption depend on the source of the raw materials, making the selection of good materials for lead-contaminated wastewater crucial [12].

Coal, a traditional high-carbon energy source in China, remains a cornerstone of the current energy supply. With the goals of carbon peak and carbon neutrality, the nation, grounded in its reliance on coal, emphasizes the effective and clean utilization of coal, enhances the capacity for integrating new energy sources, and drives the optimization of coal and new energy synergies [13]. With the reduction in high-quality coal resources and increased difficulty of extraction in recent years, brown coal, characterized by large geological reserves and lower extraction complexity, has gradually become an important component of China's energy production and supply. The colossal reserves of brown coal in China not only ensure raw material security, but also provide avenues for the materialization and purification of low-quality coal resources. Brown coal, serving as a source of humic acid (HA), is rich in oxygen-containing functional groups, capable of forming coordination bonds with heavy metals. It serves as a subsequent strengthening step in the chemical precipitation treatment of heavy metal wastewater. Constituting 25% to 45% of the elemental composition in coal-derived HAs, the diversified oxygen-containing functional groups exhibit robust electron-donating capabilities and affinity toward metal ions, and are extensively employed in the adsorption and removal of heavy metals [14].

Coal-derived HA, as a potential adsorbent for lead-containing wastewater, and its complexation with heavy metals are typically influenced by the wastewater's pH. Existing wastewater treatments show enhanced separation efficiency in weakly acidic solutions, while strongly acidic solutions may impact the separation of lead. Lead-containing wastewater is characterized by a complex multi-metal system, with  $\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Cd}^{2+}$  commonly coexisting, especially in wastewater, from lead smelting and battery discharge [2], resulting in reduced lead adsorption. Thus, comprehending the physicochemical properties of HA and heavy metals, along with summarizing effective methods to enhance the selective adsorption of  $\text{Pb}^{2+}$ , provides a theoretical basis for the preparation of adsorbents, effectively shortening the process flow. Addressing these challenges requires comprehensive reviews of HA structural identification and literature on HA–heavy metal interactions.

This review aims to address the research status of HA, providing an overview based on the molecular structure of HA from two aspects: characterization methods and separation methods, proposing the interaction mechanisms between typical structures of HA and heavy metals. Additionally, this paper explores the selective adsorption mechanism of  $\text{Pb}^{2+}$  in a multi-metal coexistence system, considering the types and physical characteristics of heavy metals in aqueous solutions, as well as the application of selective adsorbents in lead-

containing wastewater. This contributes to theoretical advancements and methodological innovations for the efficient purification of  $Pb^{2+}$ -containing wastewater.

## 2. Research Status of Molecular Structure of HA

Given the fundamental national conditions in China, where fossil energy dominates, accelerating the research, development, and widespread application of clean and efficient utilization technologies for fossil energy has become a new trend in energy transformation. Coal-based material utilization has emerged as a key aspect of this transition. Lignite, a type of coal rich in organic matter, has historically been primarily used as an energy resource. However, in recent years, lignite has gained extensive attention as a significant chemical raw material. As illustrated in Figure 1, lignite material is commonly employed in the production of carbon nanotubes, carbon dots, porous carbon materials, graphene, fullerenes, carbon fibers, humic acids (HAs) and other applications. HAs exhibit diverse structural features, including functional groups such as carboxyl, phenolic hydroxyl, aldehyde, and ketone [15]. These functional groups confer unique chemical properties to lignite-HA, forming the foundation for its extensive applications. Lignite-HA demonstrates potential value across various fields. Notably, its use as an adsorbent in water treatment is a significant application. The multitude of functional groups in lignite-HA contributes to its outstanding adsorption performance for heavy metal ions, making it a promising green material for addressing water pollution issues. Different humic substances, including humic acid, exhibit significant structural variations due to differences in their formation processes [16]. Humic substances can be categorized into HA, fulvic acid, and hmatomelanic acid based on their solubility in acidic and alkaline conditions [17]. The structural analysis of HAs, as illustrated in Figure 2, faces challenges due to their inherent heterogeneity, resulting in significant variations and incomplete structural identification.

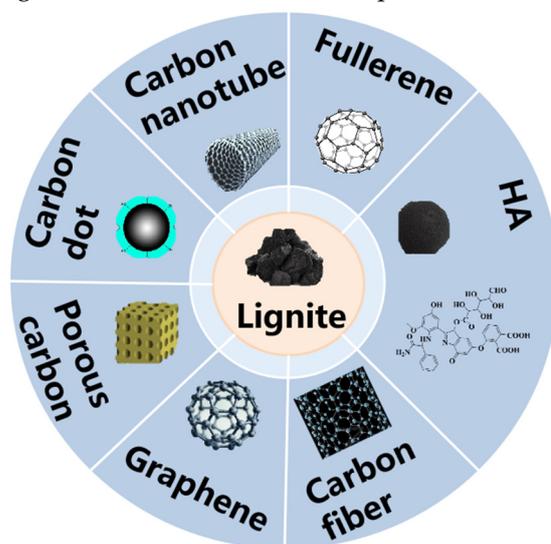
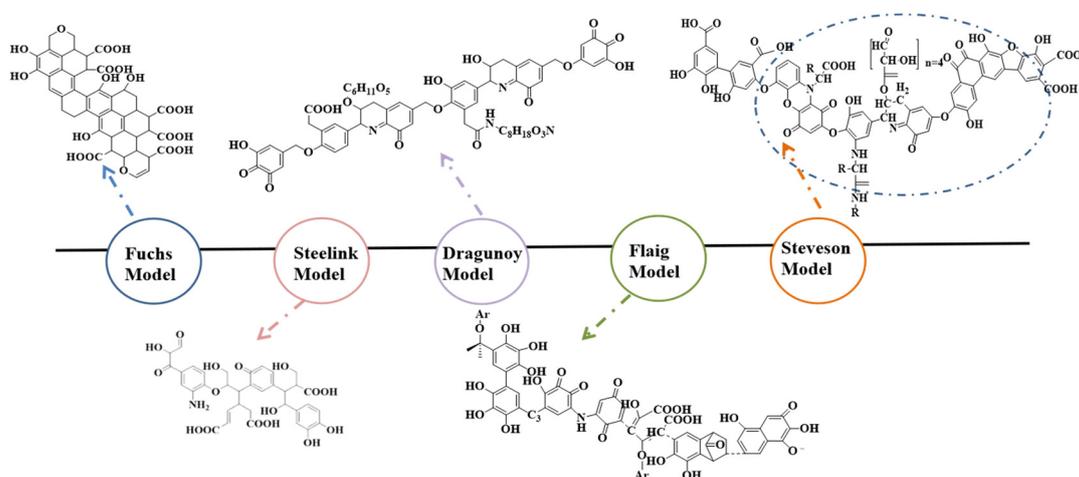


Figure 1. Application of lignite materialization.

Advancements in understanding the molecular structure of HAs have been pivotal in driving the development and refinement of characterization methods. As researchers have unraveled more complex aspects of HAs, such as their diverse functional groups, molecular size distribution, and heterogeneous composition, the need for more sophisticated and sensitive analytical techniques has become evident. This progression in molecular understanding has directly impacted the development and application of characterization methods in several ways. The first involves characterizing elemental analysis of HAs. This provides information on the carbon, hydrogen, nitrogen, sulfur, and oxygen content of HAs, offering insights into their overall composition and potential reactivity. The second involves characterizing the complex functional groups within HAs using spectroscopic techniques, such as UV-Vis spectroscopy, (Fourier-transform infrared) FTIR spectroscopy,

and nuclear magnetic resonance (NMR). These techniques analyze the overall chemical structural features of HAs. These methods have been refined to provide more detailed insights into the functional groups present in HAs, allowing for a deeper understanding of their chemical behavior and interactions in the environment. The third approach utilizes physical separation or chemical degradation methods [18], where samples are fractionated into components of varying molecular sizes or large molecules are fragmented for subsequent identification and structural analysis using spectroscopic techniques. In addition, the recognition of the wide molecular size range and structural diversity within HA populations has led to the development of more advanced chromatographic techniques, such as size-exclusion chromatography (SEC) coupled with multi-angle laser light scattering (MALLS), to accurately determine their molecular size distributions and conformational characteristics. The interaction of HAs with mineral surfaces and their role in soil and water systems have highlighted the need for advanced microscopic and surface analysis techniques, such as scanning electron microscopy (SEM) and X-ray diffraction (XRD). These techniques have been adapted to study the morphology and surface interactions of HAs, further elucidating their environmental roles.



**Figure 2.** Research status of HA molecular structure.

Understanding the chemical composition and structure of HAs is not only crucial for elucidating their origin and formation mechanisms, but also for making inferences about biomass cycling on earth and comprehending the entire geological–chemical evolutionary processes. Moreover, this knowledge holds vital significance in guiding practical applications of HAs.

## 2.1. Characterization Methods of HA Structure

### 2.1.1. Characterization of HA Elemental Composition

Analyzing and characterizing the structure and composition of HAs are fundamental to their resource utilization. The characterization of HAs typically involves elemental composition and functional group characterization [19]. Elemental composition, representing the most basic characteristics of HAs, includes common organic elements like carbon, hydrogen, oxygen, nitrogen, and sulfur. The proportions of carbon and oxygen vary with different sources, with carbon ranging from 45% to 66% and oxygen from 26% to 47%. Ratios like H/C, O/C, and N/C serve as indicators of HA's structure and types, providing insights into structural differences among various HA samples [20]. H/C represents the degree of aromatic condensation, the O/C ratio indicates the quantity of oxygen functional groups, and N/C reflects the number of nitrogen-containing groups, usually within the range of 0.02 to 0.06 [21].

### 2.1.2. Characterization of HA Functional Groups

In addition to elemental analysis, functional groups of HAs can be obtained through potentiometric titration and spectroscopic analysis. Between 68% and 91% of oxygen in HAs exists in an organic state. The sum of oxygen functional groups constitutes the total acidity of HAs (carboxylic acids, phenolic hydroxyls, quinones, methoxy groups, etc.), determining the primary active sites of HA chemical properties and biological effects [22]. Common spectroscopic analysis methods include UV-Vis spectroscopy, infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR). UV-Vis spectroscopy, with a significant structural parameter (E4/E6), serves as an indicator of the degree of aromatic condensation and the conjugation degree of other unsaturated bonds within HAs [23]. Datta et al. [24] found that soil HAs exhibit relatively higher E4/E6 values, suggesting a lower degree of aromatic compound condensation. Fatima et al. [25], through UV-Vis spectroscopy, observed changes in the functional groups of HAs in lignite before and after nitric acid treatment, discovering that the E4/E6 ratio of oxidized HAs increased, indicating higher biological activity post-oxidation.

FTIR identifies absorption peaks and quantitatively analyzes the degree of oxidation, aromaticity, and abundance of hydroxyl functional groups. Nuclear magnetic resonance technology provides an effective method for characterizing the structural composition of HA functional groups.

Solid-state NMR, based on the attribution of functional groups containing carbon, allows for the calculation of the esterification degree, aromaticity, and hydrophobicity, providing a comprehensive analysis of HA structure [26]. Verheyen et al. [27] utilized carbon spectroscopy and elemental analysis to identify HA structures, detecting an increased presence of fatty chains and aromatic rings within HAs. Ricca et al. [28] employed a range of spectroscopic methods, including UV-Vis absorption spectroscopy, FTIR, NMR, and thermal analysis, to analyze HA structures, determining an aromaticity of approximately 76% based on NMR data. Balkaş et al. [29] used similar analytical methods for characterization analysis, confirming the presence of numerous fatty chains within HAs. Novák et al. [30], through chemical and spectroscopic methods (UV-Vis absorption spectroscopy, infrared spectroscopy, and NMR), identified abundant sulfonic acid groups in HAs, detected a distinctive methoxy carbon at 55.9 ppm, and found aliphatic carbons, albeit in relatively low quantities, resulting in a calculated high aromaticity of approximately 60.6%, with a fundamental lignin skeleton. Additionally, Peuravuori et al. [31], employing similar spectral analysis, investigated the structural characteristics of South Moravian lignite and its HA component. They discovered that aliphatic compounds are tightly bound within the macromolecular network of lignite HA materials, forming complex bridging chains or complexes with hydroaromatic or polymethylene structural units.

Studies on HA structures can be categorized into destructive and non-destructive methods. The aforementioned methods for studying HA structures generally employ non-destructive techniques. Destructive pyrolysis techniques have proven valuable for obtaining detailed molecular information. Initially, Clemow et al. [32] identified HA structures at different temperatures using NMR spectroscopy and pyrolysis–gas chromatography–mass spectrometry (Py-GC/MS), observing numerous side chains, aromatic hydrocarbons, and phenolic compounds. Building upon this, Qian et al. [33] studied the structure of HAs in eastern Spanish lignite using methylated pyrolysis–mass spectrometry, identifying products of thiophene, methylthiophene, and benzothiophene, as well as benzocarboxylic acid and phenol derivatives derived from lignin. Simultaneously, aliphatic chains on the surface of HAs are readily decomposed at a low-temperature stage, with active destruction occurring in lignin and polyester-like structural domains at an intermediate stage (selective degradation process). In the advanced stage, structural rearrangement occurs in the advanced stage (simultaneous chemical decomposition and endothermic condensation). From the above references, it can be concluded that coal-derived HA structures have lignin-derived compounds as their skeletons, featuring highly condensed aromatic rings

substituted with carboxyl, phenolic, and methoxy groups. HAs, being complex, natural, organic compounds, face limitations in physical, chemical, and spectral analysis methods.

Each of these techniques (UV-Vis, FTIR, and NMR) has its advantages, but also comes with limitations and sources of error, particularly from perspectives of sample preparation and handling and sensitivity. For sample preparation and handling, in UV-Vis analysis, the solubility of the sample and the choice of solvent can affect the absorption spectrum. If the sample contains undissolved particles or is not fully homogenized, it may lead to inaccurate measurements. Sample preparation significantly impacts FTIR analysis, as the homogeneity of the sample and the thickness of the film can influence the intensity and shape of absorption peaks. Moisture in the sample can also interfere with measurements due to water's strong absorption of infrared light. NMR analysis requires the sample to have high purity. Impurities or impurity peaks from solvents may overlap with HA signals, making interpretation difficult. The concentration of the sample also needs to be precisely controlled for reproducible results. From a sensitivity perspective, UV-Vis has high sensitivity to certain functional groups, but may not provide comprehensive information about the complex structure of HAs. While FTIR can provide information about functional groups in HAs, its ability to distinguish between low concentrations and similar functional groups is limited. NMR provides the most detailed information about HA structures, but its sensitivity is limited by the sample concentration and the strength of the instrument's magnetic field. Obtaining high-quality NMR spectra for lower concentration samples can be challenging. While these characterization techniques provide valuable information regarding the structural analysis of HAs, their limitations and sources of error must be considered when using them. Understanding these limitations helps in selecting the most appropriate analytical method and in the correct interpretation of the results of the analysis. By using a combination of techniques, the limitations of a single method can be overcome, yielding a more comprehensive and accurate understanding of HA structures.

## 2.2. HA Fractionation

### 2.2.1. Methods of HA Fractionation

The significant heterogeneity and structural complexity of HAs, attributed to diverse sources and ecological systems, pose challenges to research on HAs [34]. Studies have demonstrated the fundamental importance of isolating and purifying HAs for their characterization and utilization. Current analytical methods are subsequently employed to characterize these purified HAs, enhancing our understanding of the fundamental structure and providing theoretical support for their applications.

HAs, forming macromolecular polymers through hydrophobic or hydrogen bonding interactions, present challenges in terms of heterogeneity [35]. To effectively study HAs, obtaining fractions with reduced heterogeneity through fraction becomes necessary.

Due to the presence of reactive functional groups and highly uneven distribution within HA molecules, significant differences arise in their electron-donating and electron-withdrawing tendencies. These differences result in varied solubilities in solvents with different polarities and pH values [36]. Exploiting these acid–base properties, researchers employ solubility and precipitation grading [37]. Based on the differences in solubility in hydrochloric acid, HA-like substances are divided into HA and fulvic acid fractions [38]. Wu et al. [39] proposed that pH values affect the molecular size, molecular weight, and aggregation of HAs. Fujitake et al. [40], through sequential extraction and isolation of soil HAs using phosphate solutions at different pH values, observed that increasing the pH led to a gradual increase in the H/C ratio, while the O/C and O/H ratios decreased. Additionally, the absorption intensity of aliphatic and amide groups increased, while the carboxyl group intensity decreased. Jovanovic et al. [41] explored the pH (2–11) dependency of HA particle size, finding that HAs exhibit large molecular aggregates or supramolecular structures. Klučáková et al. [42] investigated the linear relationship between functional group intensity and the dissociation ability of HAs at different pH levels. Zhang et al. [43],

through continuous alkali extraction procedures, obtained ten fractions of HA, revealing that increased extraction led to higher molecular weight, decreased carboxyl and phenolic group content, and weakened aromaticity and polarity.

Charge-based fractionation primarily involves electrophoresis, segregating solute molecules with different charges based on their differential movement rates in an electric field. HAs are negatively charged polymeric anions, and this process is typically conducted in alkaline buffer solutions. Their migration distance and speed are negatively correlated with the molecular size and positively correlated with charge density [44]. Hermosin et al. [45], utilizing thermal hydrolysis and methylation along with polyacrylamide gel electrophoresis for HAs, identified primary structures that included fatty acids and lignin. Saiz-Jimenez et al. [46], through thermal degradation of HAs, similarly obtained lignin products. Tang et al. [47], employing polyacrylamide gel electrophoresis for the fractionation of HAs and fulvic acids in water, and subsequently analyzing them through Py-GC/MS, discovered that the richest components in the largest fraction were mainly fatty acids (C16 and C18), concurrently detecting lignin-derived compounds. Despite obtaining relatively uniform HA and fulvic acid fractions through electrophoresis, this method cannot entirely prevent urea from being absorbed into the separation solution, limiting its applicability, especially in the presence of nitrogenous components.

Based on adsorption-desorption characteristics, several methods involve the use of porous silica gel, alumina, activated carbon, wood charcoal, etc., for adsorption-desorption grading. XRD-8 resin, due to its relatively weak adsorption and high desorption rate, has been proven to be an effective adsorbent for separating water-soluble organic compounds of the fulvic acid fractionation. Drosos et al. [48], employing XAD-8 resin for the fractionation of lignite HAs, observed that each fraction contained more oxygen functional groups than the original HA, which is consistent with the results of Jones [49].

Fractionation based on molecular size is one of the common methods, primarily relying on different molecular weights as grading criteria. It divides organic polydisperse systems ranging from thousands to hundreds of thousands of molecules into several molecular weight ranges [50], among which ultrafiltration is the most common. Ultrafiltration separates membranes based on pore size and is related to molecular charge and configuration. Li et al. [51], utilizing ultrafiltration technology for HA fractionation and employing elemental analysis and pyrolysis-mass spectrometry, characterized the chemical compositions of HA samples. The results showed that, with increasing molecular weight (Mw), the polarity, aromaticity, and oxygen content decreased. HAs with smaller Mw possibly originate from lignin, while those with larger Mw may originate from lipid-rich biopolymers. Tanaka et al. [52], also employing ultrafiltration technology for HA fractionation, found significant structural and compositional differences in each fraction. As the molecular weight retention decreased, the aromatic carbon content and aromaticity of each fraction gradually decreased, while the total acidity, carboxylic acid content, and fatty carbon content increased.

### 2.2.2. The Potential Impact of HA Fractionation on the Environment

HA fractionation methods play a crucial role in environmental science and soil chemistry research, yet these methods may also have potential environmental impacts. Analyzing from the perspectives of waste production, energy consumption, and chemical usage, here is a summary of the potential environmental impacts of HA fractionation: (1) Waste production: the fractionation process of HAs can generate solid waste and chemical liquids. The use of solvents for the extraction and separation of HAs results in waste liquids containing organic solvents, which, if not properly treated before discharge, can pollute water bodies and soil. Moreover, the unusable fractions produced during the fractionation process may need to be disposed of as solid waste, increasing the cost and complexity of waste management. (2) Energy consumption: the extraction and fractionation processes of HAs often require high-energy-consuming equipment, such as centrifuges, freeze dryers, and high-temperature ovens. While energy consumption may not be a major

concern for laboratory-scale studies, it can lead to a significant environmental footprint at an industrial scale, especially when the energy comes from non-renewable sources. (3) Chemical usage: the wide use of chemicals in the HA fractionation process, such as strong acids, strong bases, and organic solvents, has potential negative impacts on the environment. The production, transportation, and use of these chemicals can generate greenhouse gas emissions, and additional environmental protection measures are needed to prevent pollution during the handling and disposal of these chemicals. Selecting more environmentally friendly chemicals and optimizing the amount of chemicals used are key to reducing environmental impacts.

To mitigate the potential environmental impacts of HA fractionation, the following strategies can be adopted: (1) Optimized waste management: Reduce waste generation through waste recycling and reuse strategies, and employ environmentally friendly waste treatment and disposal methods. (2) Increased energy efficiency: Use more energy-efficient equipment and technologies to reduce energy consumption and utilize renewable energy sources as much as possible. (3) Green chemical usage: Choose more environmentally friendly solvents and chemicals; reduce the use of harmful chemicals; and employ safer, more sustainable chemical processing methods. By implementing these strategies, the environmental impact of HA fractionation can be effectively managed and mitigated, contributing to the advancement of the field towards more sustainable research and application directions.

### 2.3. The Interaction between Typical Structures of HA and Heavy Metal Ions

Understanding the adsorption mechanisms of HA on heavy metals is crucial for its practical applications. The interaction between HA and heavy metal ions is complex, owing to their heterogeneous, polyelectrolytic, and polydisperse properties. Various interactions occur, ranging from non-specific electrostatic interactions with the humic particle surface to specific interactions forming complexes and chelates with functional groups. Heavy metal ions can interact with humic substances in several ways [53], ranging from non-specific electrostatic interactions with the surfaces of humic particles to specific interactions forming complexes and chelates with functional groups [54]. The complexity arising from their structural intricacies and heterogeneity restricts the exploration of the interaction between HA and heavy metals. Based on the earlier comprehension of the molecular structure of HA, this section explores the interaction between the characteristic functional groups and the structure of HA concerning heavy metals.

HA exhibits various typical structural features, primarily characterized by functional groups like carboxyl, phenolic hydroxyl, aldehyde, and ketone. These functional groups play crucial roles in the interaction with heavy metal ions. The mechanism of the interaction between HA and heavy metals is summarized in Figure 3.

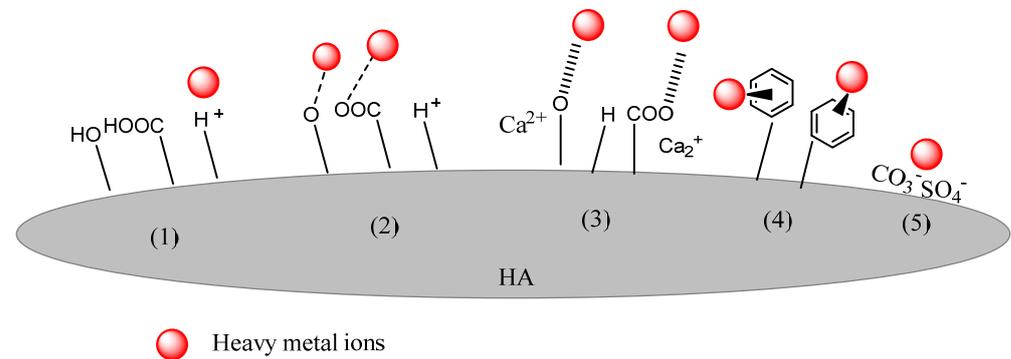
- (1) Electrostatic interaction: HA exhibits diverse pKa values, functioning as a weak acid and a strong acidic ion-exchange as a polyelectrolyte. This characteristic allows for the formation of diffuse double layers around charged particles, facilitating heavy metal adsorption [55,56]. HISS standards suggest that the content of  $-\text{COOH}$  in HA significantly exceeds that of hydroxyl groups, and their dissociation occurs at  $\text{pH} > 4.4$ , resulting in a predominantly negatively charged surface on HA [57]. This facilitates electrostatic reactions with heavy metals. At higher pH values ( $>9.5$ ),  $-\text{OH}$  become more prone to metal complexation as they are easily protonated. The increase in pH effectively deprotonates carboxylic groups, enhancing their binding with positively charged metals [58]. Studies have shown that hydroxyl and carboxyl groups in HA chelate with heavy metals, enhancing the adsorption rate [59]. Zhao et al. [44] proposed that phenolic and carboxylic groups are the primary adsorption sites for  $\text{Pb}^{2+}$ , while, according to Kinnibrugh's research [60], different functional groups exhibit varying binding affinities with metal ions, with carboxyl groups showing significant binding capacities:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ . Beyond active sites, structural features also influence the complexation of heavy metals by HA [61].

- (2) **Carboxyl Coordination and Phenolic Hydroxyl Coordination:** The carboxyl functional groups ( $-\text{COOH}$ ) in HA are important structures involved in the complexation with heavy metal ions. Heavy metal ions typically form coordination bonds with hydroxy oxygen in carboxyl groups or oxygen in carboxyl groups, resulting in the formation of stable complexes. This coordination interaction forms the basis for the selective adsorption of heavy metal ions by HA. The phenolic hydroxyl functional groups ( $-\text{OH}$ ) in HA are also key structures involved in the complexation with heavy metal ions. The oxygen atoms in these functional groups can form coordination bonds, facilitating the coordination interaction with heavy metal ions and promoting the adsorption and fixation of heavy metals.
- (3) **Ion Exchange:** Functional groups in HA possess certain ion exchange capabilities, allowing adsorption through ion exchange with heavy metal ions. This interaction is often influenced by factors such as solution pH and ion concentration.
- (4)  **$\pi$  electrons:** The  $\pi$  electrons of aromatic functional groups play a crucial role in interacting with cations, serving as  $\pi$  electron donors for the adsorption of heavy metals [62]. The cation– $\pi$  electron interaction is dependent on the aromaticity degree of the HA surface. Higher C/H ratios indicate higher aromaticity, resulting in greater electron donation capacity, reduction capacity, and adsorption capability. Li et al. [63] observed heavy metal adsorption involving cation– $\pi$  interactions, especially with corn stover biochar.
- (5) **Precipitation:** The interaction between carbonate ( $\text{CO}_3^{2-}$ ) and sulfate groups ( $\text{SO}_4^{2-}$ ) in HA and heavy metals is one of the significant behaviors of HA in the environment. These interactions generally occur through mechanisms such as coordination, ion exchange, and adsorption. (1) **Coordination:** The carboxyl and phenolic functional groups in HAs can form coordination bonds with heavy metals, resulting in the formation of complexes. The carboxyl groups on carbonate and sulfate can provide coordination sites, forming complexes with heavy metal ions, stabilizing their forms of presence, and reducing their toxicity. (2) **Ion exchange:** The carbonate and sulfate groups in Hs carry negative charges and can participate in ion exchange reactions. In the presence of heavy metal ions in the environment, they can undergo ion exchange with the carbonate and sulfate groups in HAs, being adsorbed onto the surface of HAs, thus reducing the activity and toxicity of heavy metal ions in the environment. (3) **Precipitation:** Under the influence of high concentrations of carbonate or sulfate, as well as factors such as the concentration of heavy metal ions and pH values, precipitation reactions of heavy metals with carbonate or sulfate may occur. Some heavy metal ions (such as  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ) can form carbonate precipitates with carbonate, especially under alkaline conditions. Similarly, some heavy metal ions (such as  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ) can also form sulfate precipitates with sulfate, particularly under acidic conditions.

The adsorption process of HA on heavy metals involves multiple simultaneous mechanisms, and it is intricately linked to both the chemical forms of heavy metals and the physicochemical properties of HA. Current research primarily focuses on the chelation of carboxyl and phenolic hydroxyl groups, with limited exploration of key factors influencing heavy metal adsorption. Additionally, the relationship between the physicochemical properties of HA and its adsorption of heavy metals has not been extensively studied. Therefore, elucidating this relationship holds significance for fundamental research and practical applications of HA. Moreover, research on the interaction between typical structures of HA and heavy metals has been limited to  $\pi$  electrons, with little exploration of other typical structures. Therefore, the identification of typical structures of HA holds significant importance for the study of the interaction between HA and heavy metals, as well as the design of adsorbent materials.

Overall, the interaction of carbonate and sulfate groups in HA with heavy metals through coordination, ion exchange, and adsorption regulates the migration, transforma-

tion, and bio-availability of heavy metals in the environment, playing a crucial role in reducing heavy metal pollution.



**Figure 3.** Interaction between HA and metal ions.

### 3. Selective Adsorption of Lead Ion by Coexisting System of Multiple Metals

#### 3.1. Types and Physicochemical Characteristics of Heavy Metals in Aqueous Solution

In the context of the coexistence of multiple metal ions and the treatment of complex wastewater, selectivity becomes a crucial criterion for evaluating overall adsorption performance. Adsorbents demonstrating high selectivity can effectively separate metal ions through a simple adsorption–desorption cycle. Selectivity can be achieved by modifying the surface functional groups of the adsorbent or adjusting the solution pH, thereby altering the surface charge of both the adsorbent and the adsorbate. Selective adsorption of  $\text{Pb}^{2+}$  in a multi-element coexistence system has become a focal point in the field of environmental pollution control.

Significant progress has been made in the research on the selective adsorption of  $\text{Pb}^{2+}$  in multi-element coexistence systems. Adsorption, recognized as a simple, efficient, economical, safe, and non-secondary pollution method, stands out as one of the most attractive technologies for the separation and recovery of  $\text{Pb}^{2+}$ . Various adsorption materials, including biomass materials, layered double hydroxides [64], metal–organic frameworks [65], nano-porous adsorbents [66], and carbon-based nanocomposites [67], have been synthesized and applied for the removal of  $\text{Pb}^{2+}$  from wastewater. Researchers have explored the impact of multi-element coexistence systems on the selective adsorption of  $\text{Pb}^{2+}$  by preparing different adsorption materials and employing diverse adsorption conditions. Additionally, they have investigated the influence of parameters such as solution pH and ionic strength on the adsorption of  $\text{Pb}^{2+}$  in the presence of multi-element coexistence [68,69].

Density functional theory (DFT) has been widely employed to elucidate potential adsorption mechanisms. Theoretical methods not only provide insights into the removal efficiency and binding preferences of metal ions, but also offer information on energy and geometric structure changes during the partial interactions between adsorbates and adsorbents. Theoretical studies of the adsorption process provide additional crucial advantages, such as interaction energy at different positions of the adsorbent, preferences for different metal ions, and possible interaction patterns [70]. Research on the structure and coordination characteristics of metal-adsorbent systems plays a vital role in designing and customizing new materials for the efficient removal of heavy metals from wastewater [71]. Combining theoretical research results with experimental findings has proven highly useful for understanding the mechanisms of interaction between adsorbents and metal ions during the adsorption process, as well as for synthesizing functionalized materials suitable for wastewater treatment processes [72]. Molecular dynamics simulation methods have been employed to study the competitive adsorption processes of metal ions such as  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  for  $\text{Pb}^{2+}$ , revealing that the interactions between different ions exert a significant impact on selective adsorption.

In actual heavy metal wastewater, multiple metals coexist, each with different heavy metal characteristics. Predicting metal-adsorbent interactions is facilitated by the Hard

and Soft Acid and Bases (HSAB) principle. Ionic bonds primarily form between hard metals and hard ligands, while quasi-covalent bonds exist in complexes of soft metal ligands [73]. The covalent index ( $X^2m^r$ ), based on electronegativity ( $X_m$ ) and ionic radius ( $r$ ), can be used to estimate “hardness” [74,75]. As the covalent index value increases, metal species become “softer”, resulting in stronger covalent characteristics in their bonds with ligands. Neiber et al. [76] investigated the selective adsorption of amino-phosphonates for  $Pb^{2+}$  in a multi-metal system, comparing the characteristics of various metal ions. They proposed that the main reason for the adsorbent’s selective performance is the covalent index, validating the above conclusion. In addition to the mentioned factors, the difference in the electronegativity of metal ions is also a crucial factor affecting selective adsorption. Liu et al. [77] studied the selective removal of  $Pb^{2+}$  and  $Cu^{2+}$  from water using ethylenediamine-functionalized polymer adsorbents, attributing the selective adsorption of  $Pb^{2+}$  to the difference in electronegativity between the two metal ions.

### 3.2. Application of Selective Adsorbents in Lead-Containing Wastewater

Improving the separation efficiency of specific heavy metal ions during the adsorption process is an effective approach for achieving a balance between environmental safety and economic benefits. The following provides a brief overview of common methods to enhance the selectivity for  $Pb^{2+}$ .

#### 3.2.1. Electrostatic Interaction

Electrostatic interaction, common in the environment, plays a key role in attracting heavy metals to adsorbents. The initial step involves the attraction of metal cations to the functional groups on the adsorbent surface through electrostatic forces, followed by further binding through other driving forces [78]. The efficacy of electrostatic interactions is highly influenced by the acidity of the reaction medium, primarily because the charge properties of metal species and the adsorbent surface vary at different pH values [79]. Low pH values promote the adsorption of anions, whereas an increase in solution pH results in the protonation of functional groups on the adsorbent surface due to the dissociation of  $H^+$ , creating a negatively charged adsorbent surface that is more conducive to binding metal cations. Additionally, the electrostatic adsorption process correlates with the electronegativity of heavy metal ions. Metal cations with higher electronegativity usually exhibit stronger electrostatic attraction to negatively charged sites on the adsorbent [80]. In previous study conducted by our research group [81], HA was modified using hydrogen peroxide as an oxidant to enhance the surface activity sites and charge density of HA, achieving selective adsorption of  $Pb^{2+}$ . The experimental results indicated that oxidized HA demonstrated selectivity for heavy metals in the order of  $Pb^{2+}$  (111.10 mg/g) >  $Cu^{2+}$  (76.92 mg/g) >  $Cd^{2+}$  (71.43 mg/g) >  $Ni^{2+}$  (33.33 mg/g). While the strength of the charge interaction allows for the selective separation of some ions, the selectivity is relatively weak.

#### 3.2.2. Specific Chelation Interaction

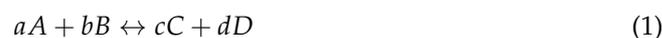
Chelation interaction is crucial for adsorbing heavy metals, with the adsorbent’s surface directly affecting its ability to capture specific metals [82]. The adsorbent surface typically contains abundant active site structures, and based on the “hard and soft acid-base theory”, oxygen-containing functional groups, amino groups, and thiol groups can effectively and selectively adsorb heavy metals. Zou et al. [83] synthesized a tannic acid-based adsorbent for heavy metal removal through self-assembly, exhibiting outstanding selectivity for  $Pb^{2+}$ , with a distribution coefficient for  $Pb^{2+}$  40–170 times higher than that of other metal ions. XPS and DFT calculations revealed that the phenolic hydroxyl groups on tannic acid served as the primary active sites, engaging in a double proton exchange mechanism after coordination with  $Pb^{2+}$ . Apart from phenolic hydroxyl groups, amino groups are also recognized as active sites for selective adsorption. Liu et al. [84] introduced multiple ligands to develop a novel metal–organic framework adsorbent, demonstrating excellent selective adsorption of  $Pb^{2+}$ . The maximum adsorption capacity of  $Pb^{2+}$  is 433.15 mg/g at

pH 5. The distribution coefficient of lead ions (26.7 L/g) shows that UiO-FHD has excellent selective adsorption for  $\text{Pb}^{2+}$ . It is revealed that the chelation of the sulfhydryl groups and the electrostatic interaction of the hydroxyl groups are the dominant factors to improve the removal rate of  $\text{Pb}^{2+}$  via density functional theory calculations. Tang et al. [85] successfully prepared a sulfur-containing amino urea metal–organic framework adsorbent for  $\text{Pb}^{2+}$  removal in wastewater. The adsorption results showed that the maximum adsorption capacity of Pb(II) is 200.17 mg/g at 303 K and optimal pH 5. Calculating the separation coefficient of interfering ions from  $\text{Pb}^{2+}$  clarified the role of amino groups in selective adsorption. The adsorption mechanism of Pb(II) on the adsorbent occurs mainly through the chelation of Pb(II) with N and S atoms. These results indicate that UiO-66-PTC is an effective material for efficiently and selectively removing Pb(II) from solution, which is of practical significance. Nankawa et al. [86] synthesized an oxalate framework adsorbent for heavy metal adsorption, and adsorption tests revealed high selectivity for  $\text{Pb}^{2+}$  compared to other heavy metals. The attributed high selectivity was linked to oxalic acid having a greater affinity for  $\text{Pb}^{2+}$ . Nuzahat et al. [87], through modeling and simulating the adsorption of  $\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Cd}^{2+}$  on HA, determined that the binding strength of the three metals followed the sequence  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ . Among these metals,  $\text{Cd}^{2+}$  posed the most significant challenging in complex with HA, consistent with the efficiency sequence of heavy metal adsorption obtained by Kerndorff [88]:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$ . The work explores the interaction process of Pb with HA through integration of synchronous fluorescence and log-transformed UV–vis absorption spectroscopy coupled with spectral slope calculation and two-dimensional correlation analyses. The spectral slope calculation results show that the carboxylic and phenolic groups in HA were the predominant binding sites to Pb, and the interaction process was highly dependent on the solution's pH. Correlation analyses confirmed a superior binding affinity of carboxylic groups in HA over phenolic groups. This indicates that, as an active site in HA, it is more conducive to the high selective adsorption of  $\text{Pb}^{2+}$ .

### 3.2.3. Ion Exchange

Ion exchange enhances metal selectivity by using the charged adsorbent surface to attract and swap metal ions [89]. Under the exchange process, ions undergo strong non-classical polarization near the solid–liquid interface under the influence of the surface electric field. Meanwhile, polarized counterions shield the surface electric field as they approach, and this interaction between ions and the surface is termed the “electric field–quantum fluctuation” coupling effect [90]. Owing to the different polarization effects of ions of the same valence but different types in an electric field, they exhibit selectivity in adsorption on charged particles [91]. The ion exchange capacity of heavy metals and adsorbents is contingent on the pH of the solution, ion composition, electronegativity of heavy metal ions, and surface chemistry of the adsorbent [92,93]. During the adsorption process, the release of other ions and changes in solution pH, usually confirmed by the occurrence of ion exchange mechanisms, are often considered.

Hofmeister effect significantly influences the adsorption behavior of ions, and this effect is commonly observed in ion exchange adsorption as well. In classical theories, the selectivity of ion exchange is correlated with the valence of ions, where higher valence states result in stronger adsorption capabilities. Existing theories attribute the Hofmeister effect to factors such as ion–ion interactions, ion volume, ion hydration effects, and dispersion forces. Table 1 presents the characteristics of common alkali (alkaline earth) metal ions. For ions of the same valence, the larger the hydrated radius, the farther the ion charge center is from the surface, leading to weaker interaction between the ion and the surface. Regarding alkali metals, the ion exchange capacity follows the order  $\text{K}^+ > \text{Na}^+$ ; for alkaline earth metals, the ion exchange capacity is ranked as  $\text{Ca}^{2+} > \text{Mg}^{2+}$ . The expression for ion exchange reactions can be represented as:



In Equation (1), *A* and *B* represent the reactants, corresponding to the solid and liquid phase components before the exchange reaction, respectively; *C* and *D* represent the products, corresponding to the chemical stoichiometry of solid and liquid components after the exchange reaction.

**Table 1.** Characteristics of common alkali and alkaline earth metal ions [94,95].

Ions	Radius (Å)	Hydration Radius (Å)	Hydration Energy (kJ mol <sup>-1</sup> )	Diffusion Coefficient (10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	Stokes Radius (nm)
K <sup>+</sup>	1.33	3.31	-295	1.957	0.124
Na <sup>+</sup>	0.95	3.58	-365	1.333	0.183
Ca <sup>2+</sup>	0.99	4.12	-1505	0.718	0.307
Mg <sup>2+</sup>	0.65	4.28	-1830	0.706	0.345

Ion exchange has been proven to be an effective method for enhancing adsorption performance. The current literature emphasizes ion exchange adsorption of heavy metals, particularly on biochar. Alkali (alkaline earth) metal ions (K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>) in biochar can exchange heavy metal ions in water [96]. Lu et al. [97] investigated the ion exchange of Pb<sup>2+</sup> in sludge-based biochar, where ion exchange accounted for 45.6–60.2% of total adsorption, with a complexation ratio of 38.2–42.4%. Zhang et al. [98] explored the adsorption mechanism of Pb<sup>2+</sup> by celery-derived biochar, indicating that ion exchange accounted for 62.8%, precipitation accounted for 34.9%, and only 2.3% was attributed to functional group complexation, achieving a high Pb<sup>2+</sup> adsorption capacity of up to 300 mg g<sup>-1</sup>. Li et al. [99] used Mg-loaded biochar for heavy metal adsorption, indicating that mineral precipitation and cation exchange played a major role in the adsorption process, with theoretical maximum adsorption values reaching 333.33 mg g<sup>-1</sup> for Cd<sup>2+</sup>, 370.37 mg g<sup>-1</sup> for Cu<sup>2+</sup>, and 302.58 mg g<sup>-1</sup> for Pb<sup>2+</sup>. Deng et al. [100], through MgCl<sub>2</sub> modification of biochar, found that the modified biochar had an adsorption capacity 2.36–9.34 times higher than that before modification, with ion exchange being the predominant adsorption mechanism. The aforementioned ion exchange applied to biomass modification has also been successfully employed for the modification and preparation of HA materials using alkaline earth metals. Sabaté et al. [94] investigated the ion exchange capacity of peat-extracted HA for 17 heavy metals, and the study found that Pb<sup>2+</sup> had the highest affinity for the ion exchange centers of HA, with the adsorption capacity for heavy metals satisfying Pb<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup>. Wang et al. [95] studied the use of Ca-loaded brown coal for the ion exchange removal of heavy metals from wastewater, and the adsorbent exhibited selectivity for Pb<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup>. This suggests that Ca<sup>2+</sup> has a stronger displacement ability for Pb<sup>2+</sup> and is more suitable for the removal of wastewater containing Pb<sup>2+</sup>. The regulation of adsorption selectivity can be achieved by changing the chemical properties of the substrate surface and controlling the nature and distribution of adsorption sites (Table 2).

**Table 2.** Cation preference for the main functional groups of natural organic matter.

Functional Groups/Ions	-COOH	-OH	-NH <sub>2</sub>	-SH	References
Na	+	N/A	N/A	N/A	[101]
Ca	++ (low pH)	+ (high pH)	+	N/A	[102]
Mg	++	+	N/A	N/A	[103]
Al	++	+	N/A	N/A	[104,105]

Note: the more symbols (+), the stronger the affinity of functional groups and structures for Na<sup>+</sup>/Ca<sup>2+</sup>/Mg<sup>2+</sup>/Al<sup>3+</sup>.

In addition to its ion exchange function, studies have demonstrated its role in activating organic functional groups. The main functional groups of natural organic matter are shown in Table 2. The cation preferences for -COOH are as follows: Ca<sup>2+</sup> ≥ Mg<sup>2+</sup> ≥ Al<sup>3+</sup> ≥ Na<sup>+</sup>. This indicates that Ca<sup>2+</sup> exhibits a higher affinity for functional groups.

The bridging role of  $\text{Ca}^{2+}$  in the organic network structure has been validated, forming a large molecular network structure of organic matter. This indicates that  $\text{Ca}^{2+}$  activates the organic functional groups [106].

#### 3.2.4. Pore Structure and Matching with Heavy Metal Size

The process of heavy metal entry into pore structures through diffusion represents a physical adsorption process, mainly influenced by pore distribution, surface electronegativity, and the characteristics of heavy metals. The capacity for heavy metals in physical adsorption and chemical adsorption increases with the adsorbent's specific surface area. The size match between adsorbent pores and metal ions is crucial for selective heavy metal adsorption. Alka et al. [107] employed amino and carboxyl-modified cuparenes and cyclodextrin decorated on nanosponges for the removal of lead-containing wastewater. The adsorption experimental results indicated that one of the reasons for the selective adsorption of  $\text{Pb}^{2+}$  is the role of the pore structure. Qiao et al. [108], by modifying the pore channels in conjugated microporous polymers with pyridine groups, efficiently removed  $\text{Pb}^{2+}$  while exhibiting high selectivity. The pore structure is one of the essential mechanisms for its selective adsorption of  $\text{Pb}^{2+}$ . Currently, there is less research on the matching effect between pore structure and heavy metal size in the study of the adsorption mechanism of heavy metals, and the interaction between them is relatively weak.

#### 3.2.5. The pH Values

pH levels directly influence how HA interacts with metals by changing the ionization of HA's functional groups, affecting metal binding and complex formation. The following are the effects of pH on the interaction between HA and metals:

**Variation in Ionization State:** Functional groups in HA, such as carboxyl and phenolic hydroxyl groups, exhibit acidity. Under different pH conditions, these functional groups may undergo ionization. At lower pH values, carboxyl and phenolic hydroxyl groups may exist in non-ionized forms, while at higher pH values, they may ionize into negatively charged ions. This change in ionization state directly affects the interaction between HA and metals.

**Stability of Complexes:** The stability of complexes formed between HA and metals is typically influenced by pH. In certain pH ranges, HA may be more conducive to forming stable complexes, while at other pH conditions, dissociation may occur. This change in stability directly influences the degree of binding between metals and HA.

**Solubility:** The solubility of metal ions under different pH conditions also changes. Under some pH conditions, metal ions may be more prone to forming precipitates or complexes with HA, whereas under other pH conditions, metal ions may be more likely to exist in a dissolved form.

Therefore, understanding the influence of pH on the interaction between HA and metals is crucial for comprehending the behavior of heavy metals in the environment and their applications in environmental remediation and wastewater treatment. pH regulation can be an effective means to control the interaction between HA and metals, enabling selective adsorption or removal under specific environmental conditions.

#### 3.2.6. Chemical Precipitation

The relationship between chemical precipitation and selective adsorption of  $\text{Pb}^{2+}$  is closely intertwined, particularly in the fields of environmental engineering and pollution control for treating lead-contaminated wastewater. Chemical precipitation removes metals by adjusting the pH and metal concentration to form insoluble complexes with the target metal [109]. Chen et al. [110] observed that phosphate precipitation, to some extent, elucidates the mechanism of selective adsorption of  $\text{Pb}^{2+}$ .

In the treatment of complex wastewater, chemical precipitation and selective adsorption can be part of a multi-stage treatment process, where chemical precipitation removes the bulk of  $\text{Pb}^{2+}$ , followed by selective adsorption for further refinement to meet lower lead

ion concentration standards. Research and development of composite materials capable of both chemical precipitation and selective adsorption can achieve effective removal of lead ions in one step, improving treatment efficiency and reducing costs.

### *3.3. The Limitations, Challenges, and Future Prospects of Selective Adsorption Mechanisms for Pb<sup>2+</sup>*

Discussing the limitations, challenges, and future prospects of selective adsorption mechanisms for Pb<sup>2+</sup> involves analyzing aspects such as electrostatic interactions, chelation, ion exchange, pore structure and its match with heavy metal sizes, pH values, and chemical precipitation.

#### 3.3.1. Limitations and Challenges of Electrostatic Interactions

**Limitations:** Electrostatic attraction highly depends on the pH and ionic strength of the solution, which may limit its application across diverse water qualities. **Challenges:** In high-salinity wastewater, background ions may shield the electrostatic attraction between the adsorbent and Pb<sup>2+</sup>, reducing adsorption efficiency. **Prospects:** Developing new adsorbent materials to enhance the specificity of electrostatic attraction for Pb<sup>2+</sup> and to minimize interference from background ions.

#### 3.3.2. Limitations and Challenges of Chelation

**Limitations:** Specific chelators may be effective only for certain metal ions, limiting their widespread application in complex wastewaters. **Challenges:** The stability and regenerability of chelating agents need further investigation for sustainable use. **Prospects:** Creating multifunctional chelators that work across a broader pH range and improve regeneration efficiency.

#### 3.3.3. Limitations and Challenges of Ion Exchange

**Limitations:** Ion exchange capacity is limited by the adsorbent's saturation, requiring replacement or regeneration after long-term use. **Challenges:** Competitive adsorption in multi-metal wastewaters may reduce selectivity for Pb<sup>2+</sup>. **Prospects:** Synthesizing new ion exchange materials with higher selectivity and larger capacity to address these issues.

#### 3.3.4. Limitations and Challenges of Pore Structure and Heavy Metal Size Matching

**Limitations:** Designing and synthesizing adsorbents with precise pore structures is complex and challenging. **Challenges:** Ensuring adsorbent pore structures effectively differentiate between metal ions of similar sizes. **Prospects:** Using nanotechnology and molecular simulations to design adsorbents with highly selective pore structures.

#### 3.3.5. Limitations and Challenges of pH Values

**Limitations:** Fluctuations in pH affect the adsorbent surface charge and the form of Pb<sup>2+</sup>, potentially limiting adsorption effectiveness. **Challenges:** Developing adsorbents that maintain high adsorption performance across a wide pH range. **Prospects:** Exploring automatic pH adjustment systems to optimize adsorption process pH conditions.

#### 3.3.6. Limitations and Challenges of Chemical Precipitation

**Limitations:** Chemical precipitation may lead to the production of secondary pollutants, necessitating additional treatment steps. **Challenges:** Balancing the efficiency and cost of precipitation reactions, especially for large-scale applications. **Prospects:** Developing more environmentally friendly and cost-effective precipitants, as well as improving precipitation processes to reduce secondary pollution.

While there are several limitations and challenges associated with selective adsorption mechanisms for Pb<sup>2+</sup>, ongoing technological innovation and material development hold the promise of overcoming these hurdles in the future, achieving more efficient and environmentally friendly Pb<sup>2+</sup> removal methods.

Table 3 above synthesizes findings from various studies on the use of HA for the removal of  $Pb^{2+}$  from different media. HA has been shown to be an effective agent for  $Pb^{2+}$  removal, leveraging mechanisms like ion exchange, complexation, and adsorption. This is a testament to the versatility of HA in treating  $Pb^{2+}$  contamination. The modification method of combining HA with nanometal materials enhances its adsorption capacity for heavy metal ions, and the modification with  $Ca^{2+}$  has verified ion exchange as an effective way to improve selectivity. The doping of  $Ca^{2+}$  has activated the adsorption active sites of HA. Concurrently, mechanistic studies have elucidated the fundamental interactions, especially the role of HA's functional groups in binding with  $Pb^{2+}$ . This is crucial for optimizing HA-based material in wastewater remediation strategies. The comparative study highlights HA's superior performance relative to other adsorbents, suggesting that HA could replace or complement existing materials in water treatment.

**Table 3.** Studies on HAs for  $Pb^{2+}$  removal.

References	Years	Modification Methods	Adsorption Capacity (mg/g)	Conclusions
[111]	2022	-	$Pb^{2+}$ : 23.11 $Cd^{2+}$ : 12.00	HA has an affinity for $Pb^{2+}$
[112]	2021	Magnetic HA nanoparticles	$Pb^{2+}$ : 105.60 $Cu^{2+}$ : 67.43 $Cd^{2+}$ : 65.23	HA exhibits selectivity for $Pb^{2+}$
[113]	2021	Calcium-modified $Fe_3O_4$ nanoparticles encapsulated in HA	$Pb^{2+}$ : 208.33 $Cu^{2+}$ : 98.33 $Cd^{2+}$ : 99.01	Ca-ion exchange is the main mechanism for the selective adsorption of $Pb^{2+}$
[106]	2023	Calcium-doped magnetic HA nano particles	$Pb^{2+}$ : 278.65 $Cu^{2+}$ : 154.31 $Cd^{2+}$ : 145.55	Ca activates the functional groups of HA
[114]	2023	-	$Pb^{2+}$ : 67.67	Carboxylic acid is the key functional group affecting the selective adsorption of HA
[115]	2012	$Fe_3O_4$	$Pb^{2+}$ : 29.00 $Cd^{2+}$ : 18.60	-
[116]	2010	Resin microspheres	$Pb^{2+}$ : 99.19 $Cu^{2+}$ : 45.80 $Cd^{2+}$ : 13.75	-
[117]	2019	Hydroxypropyl-cyclodextrin-graphene	$Pb^{2+}$ : 99.19 $Cu^{2+}$ : 45.80	-

In conclusion, while existing selective adsorption mechanisms for  $Pb^{2+}$  face several limitations and challenges, the unique characteristics of HA offer a promising outlook for its application as an adsorption material. Its potential for enhanced specificity, environmental sustainability, and economic viability in  $Pb^{2+}$  removal positions HA as a valuable resource for addressing current and future water treatment challenges.

#### 4. Conclusions

The comprehensive review and analysis of studies on HA's role in lead removal has illuminated the physical and chemical properties of HA, structural identification methods, and microscopic interactions with heavy metals. While many forms of HA demonstrate significant efficacy in binding and removing Pb from aqueous solutions, the chemical structure of HA, environmental conditions, and the physical properties of heavy metal ions affect the selective adsorption of  $Pb^{2+}$ .

Enhancements of the selective adsorption capacity for  $Pb^{2+}$  can be achieved through modifications, such as increasing activating groups, employing ion exchange, and optimizing pore structures to match the size of heavy metals. Notably, the use of  $Ca^{2+}$  has been proven to be an effective method for activating HA groups. The modifications not only increase the number of active sites available for complexation with  $Pb^{2+}$ , but also improve the stability of the resulting complexes, leading to higher removal efficiencies. Additionally, the modified HAs exhibit better performance under a wider range of environmental conditions, such as varying pH levels and the presence of competing ions, making them more versatile for real-world applications.

Future research should focus on further optimizing these HA modifications, exploring cost-effective and scalable modification processes, and evaluating the long-term sustainability and reusability of these materials in environmental remediation projects. By advancing our understanding and application of these optimized HAs, we can improve our strategies for mitigating lead pollution and protecting environmental and human health.

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